# Entropy-vanishing transition and glassy dynamics in frustrated spins

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In an effort to understand the glass transition, the dynamics of a non-randomly frustrated spin model has been analyzed. The phenomenology of the spin model is similar to that of a supercooled liquid undergoing the glass transition. The slow dynamics can be associated with the presence of extended string-like structures which demarcate regions of fast spin flips. An entropy-vanishing transition, with the string density as the order parameter, is related to the observed glass transition in the spin model.

The glass transition in supercooled liquids is heralded by anomalously slow relaxations with a time scale diverging as the liquid freezes into the glassy state [1]. In recent years, there have been careful experimental and theoretical studies aimed at understanding the structural aspects of this transition. The presence and nature of dynamical heterogeneities near the glass transition has been a dominant underlying theme of both simulations [2,3] and experiments [4,5]. Simulations in Lennard-Jones liquids [2] have shown the existence of string-like dynamical heterogeneities and similar structures have been observed directly in colloidal glasses [5]. In the Adam-Gibbs scenario, the glass transition is related to a phase transition accompanied by the vanishing of configurational entropy [6,7]. An explicit connection between (a) dynamical heterogeneities, (b) anomalous relaxations and (c) the Adam-Gibbs scenario would provide useful insight into the nature of the glass transition. In this work, we present our analysis of a simple model where there are naturally occurring dynamical heterogeneities in the form of strings and where there is an entropy vanishing transition involving these structures. Monte Carlo simulations of the model show that there is a glass-like transition with diverging time scales and an anomalously broad relaxation spectrum. Analysis of the simulation results provides strong evidence that the entropy-vanishing transition underlies the observed dynamical behavior.

*a. Model* One of the simplest non-randomly frustrated spin models is the triangular-lattice Ising antiferromagnet (TIAFM). The TIAFM has an exponentially large number of ground states and has a zero-temperature critical point [8–10]. The model studied in this letter is the *compressible* TIAFM (CTIAFM) in which the coupling of the spins to the elastic strain fields removes the exponential degeneracy of the ground-state. We solve the CTIAFM exactly within the ground-state ensemble of the TIAFM and show that there is an entropy-vanishing transition which involves extended structures. We then present results of simulations which indicate that the entropy-vanishing transition leads to glassy dynamics.

The Hamiltonian of the CTIAFM is:

$$H = J\sum_{<ij>} S_i S_j - \epsilon J \sum_\alpha e_\alpha \sum_{<ij>_\alpha} S_i S_j + N\frac{E}{2}\sum_\alpha e_\alpha^2 \ . \quad (1)$$

Here $J$, the strength of the anti-ferromagnetic coupling, is modulated by the presence of the second term which defines a coupling between the spins and the homogeneous strain fields $e_\alpha, \alpha = 1, 2, 3$, along the three nearest-neighbor directions on the triangular lattice. The last term stabilizes the unstrained lattice. The total number of spins in the system is given by $N$. The ground-state of the CTIAFM is a three-fold degenerate striped phase where up and down spins alternate between rows and there is a shear distortion characterized by $e_1 = e$ and $e_2 = e_3 = -e$ if the rows are along the direction of $e_1$ [11,12]. Within the manifold of the TIAFM ground-states, the competition between energy gained from the lattice distortions and the extensive entropy of the TIAFM ground-states leads to an entropy-vanishing transition. The order parameter associated with this entropy-vanishing transition is the density of extended string-like structures which characterize the TIAFM ground states.

The string picture of the TIAFM ground states derives from a well-known mapping of these states to dimer coverings [13,14]. In a ground state, there is one unsatisfied bond per triangular plaquette and the dimers are the filled-in bonds of the dual honeycomb lattice that cross the unsatisfied bonds of the triangular lattice, as shown in Fig.(1). Superposing a dimer configuration on a "standard" dimer configuration where all the dimers are vertical [13,14] leads to a string configuration (*cf* Fig.(1)). Assuming spin-flip dynamics for the moment, the only spins that can be changed while the system remains in the ground-state manifold, are the ones which have a coordination of 3-3 (3 satisfied and 3 unsatisfied bonds). These are the fast spins in the system, and, as shown in Figure (1), are located at isolated kinks on the strings. The strings, therefore, play the role of dynamical heterogeneities in this lattice model.

*b. Exact results* We can solve the CTIAFM exactly within the restricted spin ensemble of the ground states

of the TIAFM. All the states in this ensemble can be classified according to the string density $p = N_s/L$ where $L$ is the linear dimension of the sample and $N_s$ is the number of strings [13]. The number of spin states ($\Omega(p)$) belonging to a particular string-density sector $p$ has been shown to be exponentially large [13]: $\Omega(p) = \exp(N\gamma(p))$, with $N = L \times L$ being the total number of spins. As shown in Fig. (2), the entropy $\gamma(p)$ has a peak at $p = 2/3$ [13]. In the CTIAFM (Eq. 1), the strain $e_\alpha$ couples to $\langle S_i S_j \rangle_\alpha$. This average counts the number of strings along the $\alpha$ direction, *i.e.* the number of strings obtained by taking an overlap with the standard dimer state with all the dimers perpendicular to the $\alpha$ direction. Under periodic boundary conditions, only one of the three string densities is independent.

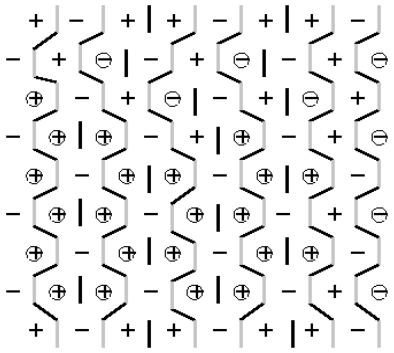

FIG. 1. String representation of a TIAFM ground state. Dark bonds of the dual honeycomb lattice (*cf* text) are the dimers which divide unsatisfied pairs of spins. Light bonds define the "standard" dimer configuration. The strings are made up of these two types and extend across the system. The fast spins, the ones with $3-3$ coordination, have been encircled.

The strain field appears in the Hamiltonian as a purely Gaussian variable and can be integrated out, and the CTIAFM energy per spin, *in the restricted ensemble*, can be written in terms of the one, independent string density $p$:

$$E(p) = -(\mu/2)((1-2p)^2 + 2(1-p)^2)) \ . \qquad (2)$$

Here $\mu = \epsilon^2 J^2/E$. The energy function $E(p)$ distinguishes different string sectors and is minimized by $p = 0$. The entropy of the ground states, $\gamma(p)$, on the other hand favors the $p = 2/3$ sector and the competition between energy and entropy leads to the possibility of a phase transition. In the thermodynamic limit, the partition function $Z = \sum_p \exp^{-Nf(p)}$, is dominated by the string density which minimizes $f(p) = \beta E(p) - \gamma(p)$, where $\beta$ is the inverse temperature. The exact free energy corresponds to this minimum value of $f(p)$ and the only relevant coupling constant in the problem is $\beta\mu$. For small values of the coupling constant, the function $f(p)$ shown in Fig (2(b)), has only one minimum at $p = 2/3$. As the coupling constant is increased, this minimum stays pinned at $2/3$ and a second minimum starts developing at $p = 0$. The $p = 0$ state stays metastable until at $\mu/T_1 = (3/4) * \gamma(2/3) \simeq 0.24$ there is a first-order transition from the $p = 2/3$ state to the $p = 0$ state. The $p = 2/3$ state loses its metastability at a larger coupling given by $\mu/T^* = \sqrt{3}\pi/12$. At $T^*$, the entropy vanishes and the order parameter shows a discontinuous change from $p = 2/3$ to $p = 0$. This transition is reminiscent of the transitions observed in p-spin spin glasses [7,16].

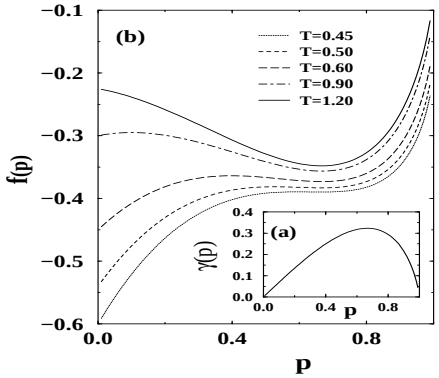


FIG. 2. (a) Entropy as a function of the string density from the work of Dhar et al.( [13]) (b)The dimensionless free energy $f(p)$ for $\mu = 0.18$. $T^*$ for this value of $\mu$ is 0.397. Temperature is measured in units of $1/k_B$.

These exact results show that in the CTIAFM, there is an entropy vanishing transition which defines the limit of stability of the homogeneous, liquid-like $p = 2/3$ state. In the Adam-Gibbs scenario, such a transition underlies the glass transition. The exact results are valid for the CTIAFM acting within the ground-state ensemble of the TIAFM. Defects [15], which correspond to triangles with all three bonds unsatisfied, can take the system out of the ground-state manifold. For low defect densities, however, it is possible that the entropy-vanishing transition survives in some form and leads to slow glassy dynamics. We have investigated this scenario by performing Monte Carlo simulations of the CTIAFM.

*c. Simulations* The parameters of the model were chosen to be $J = 1$, $\epsilon = 0.6$ and $E = 2$. These values yield a small value of $\mu$ ($= 0.18$) and ensures that at the transition, $T^*$ ($= 0.397$), the defect density is low. The average defect number-density was measured to be $\simeq 0.04\%$ at $T = 0.45$. We used Monte Carlo simulations to study the dynamics of the supercooled state following instantaneous quenches to temperatures below $T_1 = 0.75$. Spin-exchange kinetics was extended to include moves which attempted changes of the strain fields $e_\alpha$. Details of the simulation algorithm have been published earlier [12]. System sizes ranged from 48x48 up to 120x120. Unless otherwise stated, the results presented in this letter were obtained from 96x96 systems.

As the glass transition is approached, global quantities

such as the energy per spin should exhibit anomalously slow relaxation processes. Fig (3) shows the energy autocorrelation function $C_E(t,t_0) =< E(t_0)E(t+t_0) >$. For quench temperatures between $T = 0.6$ and T=0.47, $C_E(t,t_0)$ is *independent* of the time origin $t_0$ and has a stretched exponential form; $\exp^{-(t/\tau_E)^\beta}$. The stretching-exponent $\beta$ decreases from 0.45 to 0.35 over this temperature range and the time scale $\tau_E$ increases rapidly as is evident from the top panel of Fig (3). Below $T \simeq 0.47$, the energy autocorrelation function depends on the time origin $t_0$, indicating that the equilibration times have become longer than our observation times. To illustrate the dependence on the waiting time $t_0$, we have shown the autocorrelation function averaged over three different ranges of $t_0$ at $T = 0.45$. The system is seen to relax more slowly for longer waiting times $t_0$. This behavior of the energy autocorrelation function is similar to that of supercooled liquids and the temperature $T = 0.47$ is analogous to the laboratory glass transition temperature at which the equilibration time becomes longer than the observation time. In the CTIAFM, the proximity of this transition to $T^*$ suggests that the glassy dynamics is related to the entropy vanishing transition.

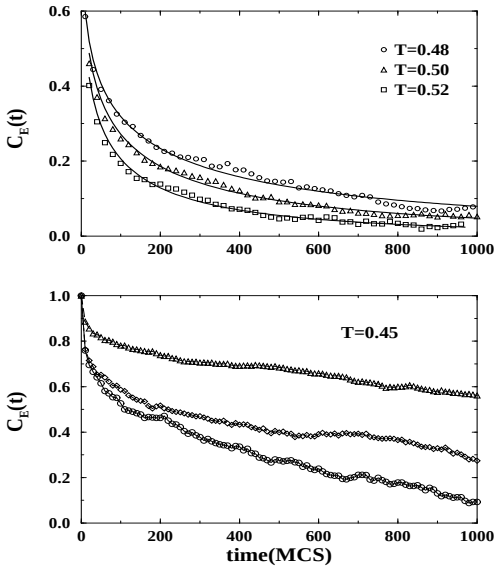


FIG. 3. Top frame shows $C_E(t,t_0)$ for three different temperatures where $C_E(t,t_0)$ does not depend on $t_0$. The solid lines are stretched exponential fits. Bottom frame shows the waiting-time dependence of the energy autocorrelation function at $T = 0.45$. The curves were obtained by averaging $C_E(t,t_0)$ over three different ranges of $t_0$. From bottom to top, these ranges are $0 < t_0 < 25000$, $18000 < t_0 < 48000$ and $50000 < t_0 < 80000$.

The microscopic picture of the entropy-vanishing transition is one where the string density vanishes. An analysis of the string-density relaxation can, therefore provide some insight into the nature of the dynamics at the glass transition. We find that the string-density autocorrelation functions are well described by exponential relaxations, in contrast to the energy autocorrelation functions. Fig. (4) shows the results of our simulations for the relaxation times and fits to a power-law and a Vogel-Fulcher form [17]. Both fits yield a time-scale divergence at a temperature $T \simeq T^*$. The $\tau_E$ obtained from the stretched exponential fits to $C_E(t,t_0)$ has a temperature dependence which tracks that of the string relaxation time. This observation suggests that the slow, non-exponential relaxations are a consequence of the freezing of the string-density relaxation which, in turn, is related to the entropy vanishing transition. The static susceptibility associated with the string density changes only by a factor $\simeq 2$ over the temperature range in which the time scales change by a factor $\simeq 40$, indicating that the entropy-vanishing transition suffers from anomalously strong critical slowing down.

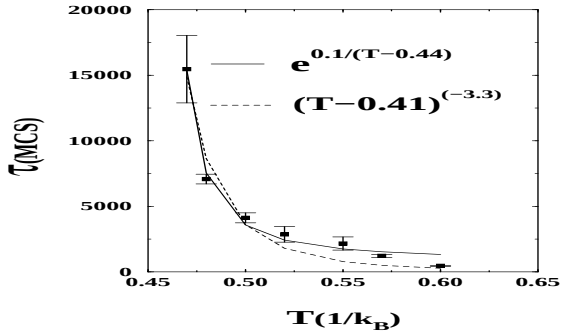


FIG. 4. Temperature dependence of the string-density relaxation time. The simulation results are shown with error bars. The solid line is a fit to the Vogel-Fulcher form and the dashed line to a power-law.

In order to investigate the nature of the string-relaxations further, we measured the distribution, $P(\Delta p)$, of $\Delta p = p(t+t_0) - p(t_0)$, the deviation of the string density in the time interval $t$ (Fig. (5)). The distributions were generated by choosing different time origins $t_0$. The most striking feature of the distributions, observed at temperatures close to $T = T^*$, is its non-Gaussian nature at intermediate times. At $T = 0.55$, the non-Gaussian feature is most pronounced at $t = 4000$. Beyond this time the distribution relaxes towards a Gaussian and for $t \geq 8000$, the distribution is time independent. At $T = 0.47$, a time-independent behavior is not observed for times as long as 30,000 and the distributions are non-Gaussian at all intermediate times. In usual critical-point dynamics [18], one would expect to find a distribution of $\Delta p$ which takes longer to reach its time-independent form as the critical point is approached and to find non-Gaussian behavior (within the limits of finite-size cutoffs) in the stationary distribution. In contrast, we observe the most pronounced non-Gaussian features at intermediate times. Drawing an analogy with critical

phenomena, this observation leads us to speculate that there exists a time-dependent length scale, $\xi(\tau)$ has a peak at a time $\tau_0(T)$. As $T \to T^*$, the time scale $\tau_0$ and the height of the peak, $\xi(\tau_0)$ appear to diverge. The exact nature of the divergence is difficult to extract from the current data. These apparent divergences indicate that the thermodynamic transition present in the zero-defect sector has been replaced by a dynamical transition [19].

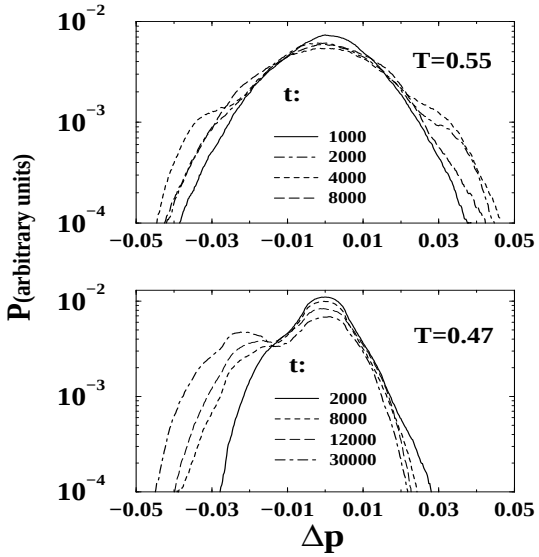


FIG. 5. Distribution of string-density deviation $\Delta p$ for different time intervals, $t$, shown at $T = 0.55$ and $T = 0.47$. The areas under the curves have been normalized to unity.

*d. Connection to real glasses* In conclusion, our study of the CTIAFM provides strong indication that the slow, glassy dynamics in this model is associated with an entropy-vanishing transition involving extended, string-like structures. These structures are a manifestation of the frustration embodied in the nearest-neighbor, antiferromagnetic interactions, and the entropy-vanishing transition is a consequence of coupling to another degree of freedom, the lattice strain, which tends to remove the frustration in the system. The strings are naturally occurring dynamical heterogeneities since they demarcate regions of fast spin flips. If the relation between frustration and dynamical heterogeneities is a generic feature of glass formers, then our observations would suggest that the clusters of mobile particles observed in Lennard-Jones simulations [2] and in colloidal systems [5] should consist of the most frustrated particles in the system. In a Lennard-Jones mixture, these should be the particles with the least number of unlike bonds (if unlike bonds are energetically preferred) and in a colloidal system, these should be the particles which have coordinations that are furthest from being icosahedral. An experimental verification of this correlation between geometry and mobility would be a direct test of the connection between the glass-transition and an entropy-vanishing transition involving extended structures forced in by frustration.

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